

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
28 July 2005 (28.07.2005)

PCT

(10) International Publication Number  
**WO 2005/068399 A1**

BEST AVAILABLE COPY

- (51) International Patent Classification<sup>7</sup>: **C04B 41/45**,  
C08K 3/34, 5/54, 5/541, C09D 183/04, 183/02, 185/00
- (21) International Application Number:  
PCT/AU2005/000042
- (22) International Filing Date: 14 January 2005 (14.01.2005)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
2004900174 15 January 2004 (15.01.2004) AU
- (71) Applicant (for all designated States except US):  
**UNISEARCH LIMITED** [AU/AU]; Rupert Myers  
Building, Gate 14, Barker Street, UNSW, Sydney, New  
South Wales 2052 (AU).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **ZHANG, Hua**  
[AU/AU]; School of Chemistry, University of New South  
Wales, SYDNEY, New South Wales 2052 (AU). **LAMB,**  
**Robert Norman** [AU/AU]; School of Chemistry, Univer-  
sity of New South Wales, SYDNEY, New South Wales  
2052 (AU).
- (81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,  
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,  
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,  
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,  
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,  
ZW.
- (84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,  
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,  
FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO,  
SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,  
GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF MAKING A SURFACE HYDROPHOBIC

(57) Abstract: The present invention provides a method for rendering a microstructured surface of a substrate hydrophobic. The method comprises a first step of applying to the microstructured surface a coating composition capable of forming a hydrophobic coating having a nanoscale roughness on the microstructured surface. The composition is then cured to form a hydrophobic coating having a nanoscale roughness on the microstructured surface. The resultant surface has both nanoscale roughness and microscale roughness.

WO 2005/068399 A1

- 1 -

## METHOD OF MAKING A SURFACE HYDROPHOBIC

## TECHNICAL FIELD

The present invention relates to methods for rendering  
5 surfaces hydrophobic.

## BACKGROUND ART

Hydrophobic surfaces, and in particular superhydrophobic  
surfaces, have many advantageous properties. Hydrophobic  
10 surfaces are water proof or water resistant.

Superhydrophobic surfaces also display a "self-cleaning"  
property, in which dirt or bacteria, spores and other  
microorganisms that come into contact with the surface  
cannot readily adhere to the surface and are readily  
15 washed away by water. Superhydrophobic surfaces are also  
resistant to attachment by water-soluble electrolytes,  
such as acids and alkalies, and are also resistant to  
icing and fouling.

20 The standard method for measuring the hydrophobicity of a  
surface is to measure the contact angle  $\theta$  of a droplet of  
water on the surface. A surface is usually considered to  
be hydrophobic if the contact angle of water is greater  
than  $90^\circ$ . Coatings on which water has a contact angle  
25 greater than  $90^\circ$  are referred to as hydrophobic coatings.  
Surfaces with water contact angles greater than  $130^\circ$  are  
commonly referred to as superhydrophobic surfaces.  
Similarly, coatings on which water has a contact angle  
greater than  $130^\circ$  are commonly referred to as  
30 superhydrophobic coatings.

If a surface is rough or heterogeneous, there are usually  
two contact angles that can be measured. Tilting the

- 2 -

surface until the droplet is about to roll off illustrates this phenomenon. The contact angle of the leading edge of the droplet represents the largest measurable contact angle and is called the advancing contact angle or  $\theta_{adv}$ .

5 The contact angle of the receding edge of the droplet represents the minimum measurable contact angle and is called the receding contact angle or  $\theta_{rec}$ . The difference between the advancing and receding contact angles is known as the contact angle hysteresis and defines the degree of

10 dynamic wettability.

The contact angle hysteresis of water indicates the stability of a droplet of water on the surface, the lower the contact angle hysteresis the less stable the droplet

15 is and therefore the easier the water droplet slides off the surface.

Methods of forming superhydrophobic coatings, and applying superhydrophobic coatings to surfaces, have been described

20 in the prior art. For example, WO 98/42452 and WO 01/14497 describe methods of forming superhydrophobic coatings. However, the superhydrophobic coatings formed by the methods described in WO 98/42452 and WO 01/14497 have a number of disadvantages, and in particular are generally

25 easily damaged and removed from the surface to which they are applied.

In view of the many practical advantages of rendering surfaces hydrophobic, it would be advantageous to develop

30 alternative methods of rendering the surfaces of a substrate hydrophobic.

- 3 -

**DISCLOSURE OF THE INVENTION**

The present inventors have unexpectedly found that a microstructured surface may be rendered hydrophobic by overlaying the microstructured surface with a hydrophobic coating having a nanoscale roughness, and that the resultant coated surface has a greater hydrophobicity than a non-microstructured surface overlayed with the same hydrophobic coating.

10 Accordingly, in a first aspect, the present invention provides a method for rendering a microstructured surface of a substrate hydrophobic, the method comprising the steps of:

- applying to the microstructured surface a coating composition capable of forming a hydrophobic coating having a nanoscale roughness on the microstructured surface; and then
- curing the composition to form a hydrophobic coating having a nanoscale roughness on the microstructured surface, such that the resultant surface has both nanoscale roughness and microscale roughness.

In some embodiments of the present invention, a surface of a substrate is treated to form a microstructured surface on the substrate prior to applying to the microstructured surface the coating composition capable of forming a hydrophobic coating having a nanoscale roughness.

Accordingly, in a second aspect, the present invention provides a method for rendering a surface of a substrate hydrophobic, the method comprising the steps of:

- treating the surface of the substrate to form a microstructured surface;

- 4 -

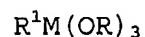
- applying to the microstructured surface a coating composition capable of forming a hydrophobic coating having a nanoscale roughness on the microstructured surface; and then
  - 5 - curing the composition to form a hydrophobic coating having a nanoscale roughness on the microstructured surface, such that the resultant surface has both nanoscale roughness and microscale roughness.
- 10 The surface of the substrate may be physically treated to form a microstructured surface. Alternatively, the surface may be treated by applying a coating composition to the surface to form a coating on the surface, wherein the coating has a microstructured surface.

15

Preferably the resultant surface is superhydrophobic.

In some embodiments, the coating composition capable of forming a hydrophobic coating having a nanoscale roughness

20 comprises one or more compounds of the formula (A):



(A)

25 wherein:

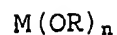
$R^1$  is a non-polar group,

M is a metal, and

each R is independently selected and is an alkyl group,

30 optionally together with one or more additional compounds selected from the group consisting of compounds of the formula (B) and compounds of the formula (C):

- 5 -



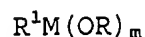
(B)

wherein:

M is a metal,

5 each R is independently selected and is an alkyl group,  
and

n is 3 or 4;



10

(C)

wherein:

 $R^1$  is a non-polar group,

M is a metal,

15 each R is independently selected and is an alkyl group,  
and

m is 1 or 2.

20 In formulas (A), (B), and (C), R is typically a  $C_{1-10}$  alkyl,  
such as methyl, ethyl, propyl, etc.

In formula (A), M is typically Si or Zn, more typically Si. In formula (B), M is typically Si, Zn or Al. In formula (C), M may for example be Al or Zn. Compounds of  
25 formula (C) include, for example, compounds of the formula  $R^1Al(OR)_2$  or  $R^1Zn(OR)$ .

In formulas (A) and (C),  $R^1$  may be any non-polar group.  $R^1$  is typically  $C_{1-10}$  alkyl,  $C_{2-10}$  alkenyl, phenyl, an epoxy  
30 group, an acrylate group or an isocyanate group. When  $R^1$  is an alkyl, alkenyl or phenyl group, the alkyl, alkenyl or phenyl group may be optionally substituted by one or more non-polar groups.

- 6 -

The compound of formula (B) may for example be a tetraalkoxysilane, such as tetraethyl orthosilicate ( $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ ) or tetramethyl orthosilicate ( $\text{Si}(\text{OCH}_3)_4$ ).

- 5 The hydrophobic coating having a nanoscale roughness is formed by the compounds of formula (A) (and optionally compounds of formulas (B) and (C)) reacting together in a modified sol-gel reaction.
- 10 In preferred embodiments, the coating composition capable of forming a hydrophobic coating having a nanoscale roughness comprises one or more tri-functional alkylsilanes, and the hydrophobic coating having a nanoscale roughness is formed by the molecules of the tri-
- 15 functional alkylsilanes reacting together in a modified sol-gel reaction. Preferably, the coating composition comprises two or more different tri-functional alkylsilanes, the different alkylsilanes having different length alkyl chains. For example, in some embodiments,
- 20 one of the tri-functional alkylsilanes in the coating composition has an alkyl chain having a length of 3 or less carbon units (i.e. a  $\text{C}_{1-3}$  alkyl), and another of the tri-functional alkylsilanes in the coating composition has an alkyl chain having a length of 6 or more carbon units
- 25 (eg. a  $\text{C}_{6-30}$  alkyl).

The coating composition comprising the one or more tri-functional alkylsilanes may further comprise a polymer that is capable of chemically bonding to the tri-

30 functional alkylsilane(s) and to the microstructured surface. Preferably, the polymer is a polysiloxane polymer. The coating composition typically further comprises an organic solvent, such as ethyl acetate, butyl

- 7 -

acetate, toluene, xylene, methyl ethyl ketone, acetone, hexane, light petroleum, diethylether, or tetrahydrofuran.

When a coating composition comprising the one or more tri-  
5 functional alkylsilanes is used in the method of the present invention, the composition is typically cured by allowing the composition to dry at room temperature (eg. about 15°C to about 30°C) in the presence of air. However, in some embodiments, curing of the composition  
10 may comprise exposing the composition to elevated temperatures, for example, up to about 60 or 80°C.

Preferably the contact angle of water on the resultant hydrophobic surface (i.e the coated surface) is greater  
15 than 130°, more preferably greater than 150°, and even more preferably greater than 160°.

In a third aspect, the present invention provides a hydrophobic surface produced by the method of the first or  
20 second aspects of the present invention.

In a fourth aspect, the present invention provides a superhydrophobic surface produced by the method of the first or second aspects of the present invention.  
25

In a fifth aspect, the present invention provides an article having at least one surface that has been rendered hydrophobic by the method of the first or second aspects of the present invention.  
30



- 8 -

**MODES FOR CARRYING OUT THE INVENTION**

The method of the present invention produces a surface having both a nanoscale and microscale roughness (ie. the resultant surface is both microstructured and  
5 nanostructured). The combination of the microstructured surface and the overlying hydrophobic coating having a nanoscale roughness results in surfaces having a greater hydrophobicity than non-microstructured surfaces overlayed with the same coating.

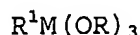
10

**Coating composition**

Any coating composition that is capable of forming a hydrophobic coating having a nanoscale roughness on the microstructured surface may be used in the method of the  
15 present invention.

In some embodiments of the present invention, the coating composition comprises hydrophobic nanoparticles or nanoparticles that are capable of being rendered  
20 hydrophobic during curing of the composition. In other embodiments, the coating composition comprises precursors capable of reacting during the curing of the composition to form hydrophobic nanoparticles. In these embodiments, the nanoscale roughness on the resultant surface is  
25 provided by the hydrophobic nanoparticles.

In some embodiments, the coating composition comprises hydrophobic nanoparticles formed by a hydrolysis and condensation reaction between one or more compounds of the  
30 formula (A):



(A)

- 9 -

wherein:

$R^1$  is a non-polar group,

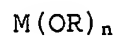
M is a metal, and

each R is independently selected and is an alkyl group,

5

optionally together with one or more additional compounds  
selected from the group consisting of compounds of the  
formula (B) and compounds of the formula (C):

10



(B)

wherein:

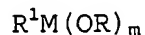
M is a metal,

each R is independently selected and is an alkyl group,

15

and

n is 3 or 4;



(C)

20

wherein:

$R^1$  is a non-polar group,

M is a metal,

each R is independently selected and is an alkyl group,

25

and

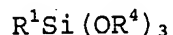
m is 1 or 2.

The hydrolysis and condensation reactions are a modified  
sol-gel reaction. The hydrophobic nanoparticles can be  
30 prepared by reacting the compounds of formula (A) and  
optionally (B) and (C) in an organic solvent in the  
presence of a catalyst and a small quantity of water to  
initiate the hydrolysis reaction.

- 10 -

In some embodiments, the coating composition comprises compounds of formula (A) (and optionally compounds of formulas (B) and (C)), which are capable of reacting together by hydrolysis and condensation reactions to form hydrophobic nanoparticles. In these embodiments of the present invention, during the curing of the coating composition, the solvent in the coating composition is removed from the composition, and the compounds of formula (A), (B) and (C) present in the coating composition react to form hydrophobic nanoparticles, which bind to each other and to the surface, to thereby form a hydrophobic coating having a nanoscale roughness on the microstructured surface.

In preferred embodiments of the present invention, the coating composition comprises one or more tri-functional alkylsilane(s). Tri-functional alkylsilanes are compounds having a silicon atom bonded to an alkyl group and three functional groups capable of undergoing hydrolysis and condensation reactions. Such compounds include tri-alkoxy alkylsilanes of the general formula



wherein:

$R^1$  is an alkyl group, typically a  $C_{1-30}$  alkyl, and each  $R^4$  is independently selected and is an alkyl group, typically a  $C_{1-3}$  alkyl.

Under suitable conditions, tri-functional alkylsilanes are capable of reacting by a modified sol-gel reaction to form a hydrophobic coating having a nanoscale roughness. The resultant coatings are extremely hydrophobic because the

- 11 -

reacted alkylsilane has a hydrophobic alkyl group. For simplicity, the modified sol-gel reaction will now be described in more detail in relation to tri-functional alkylsilanes. However, similar reactions also occur  
5 between the compounds of formulas (A), (B) and (C), as defined above.

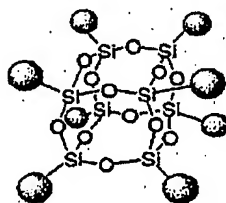
In a modified sol-gel reaction, the tri-functional alkylsilane reacts to form nanoscale sized covalently  
10 bonded networks of reacted alkylsilanes, such as the silsesquioxane or amorphous polysilsesquioxane, or "ormosil", shown below. Ormosil is an acronym for organically modified sols.

15 The nano-sized covalently bonded networks of reacted alkylsilanes are hydrophobic nano-sized particles. For convenience, the nanoscale sized covalently bonded networks of reacted alkylsilanes will be referred to below as hydrophobic nanoparticles.

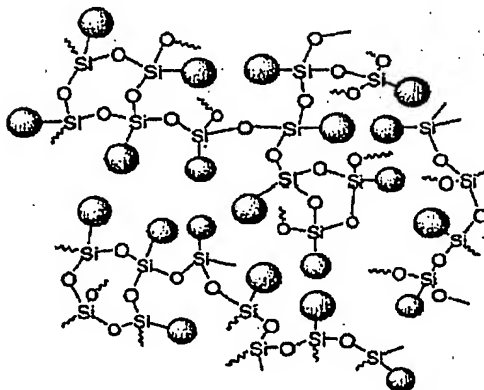
20

● ⇔ Alkyl group

$(R'O)_3Si-$



Silsesquioxane



Ormosil

- 12 -

The nanoscale sized covalently bonded networks of reacted alkylsilanes may be joined to other nanoscale sized covalently bonded networks of reacted alkylsilanes to form a covalently bonded network of hydrophobic nanoparticles.

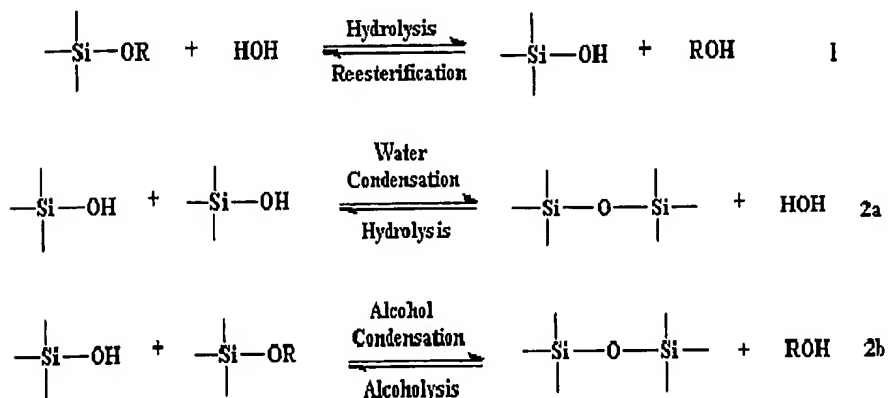
- 5 On curing, during which any solvents present are removed, a covalently linked network of hydrophobic nanoparticles is formed, producing a hydrophobic coating having a nanoscale roughness on the surface. During this process, the nanoparticles may form agglomerations.

10

The modified sol-gel reaction consists of two main reactions:

- Hydrolysis: where a reactive functional group (for example an alkoxy group in the case of a tri-alkoxy alkylsilane) of the tri-functional alkylsilane is hydrolysed; and  
 15 Condensation: where the hydrated tri-functional alkylsilane reacts with another optionally hydrated tri-functional alkylsilane to form a covalently bonded network.

20



These two reactions are usually concurrent.

- 13 -

In a preferred embodiment of the present invention, the coating composition comprises one or more tri-functional alkylsilane(s), a polysiloxane compound capable of reacting with the alkylsilane(s), an organic solvent, and  
5 a catalyst. The present invention will be described in more detail below by reference to this embodiment of the invention. For convenience, tri-functional alkylsilanes will simply be referred to below as "alkylsilanes".

10 When such a coating composition is applied to the microstructured surface and exposed to water in the atmosphere, a modified sol-gel reaction occurs forming the hydrophobic coating having a nanoscale roughness. During this process, the alkylsilanes undergo hydrolysis and  
15 condensation reactions as discussed above, forming hydrophobic covalently bonded networks (hydrophobic nanoparticles).

The alkylsilane may be any alkylsilane having three  
20 functional groups which are capable of undergoing hydrolysis and condensation reactions. Suitable functional groups include acetoxy, enoxy, oxime, alkoxy and amino. The three functional groups on a tri-functional alkylsilane may be the same or different.

25 The alkyl group on the alkylsilane may be straight chain or branched and may be, for example, methyl, ethyl, propyl, butyl or octyl.

30 Preferably, the three functional groups are all alkoxy (i.e. the alkylsilane is a tri-alkoxy alkylsilane). Specific tri-alkoxy alkylsilanes for use in the present invention include methyltrimethoxysilane,

- 14 -

methyltriethoxysilane, ethyltrimethoxysilane,  
ethyltriethoxysilane or octyltriethoxysilane.

In preferred embodiments of the present invention, the  
5 coating composition comprises two or more alkylsilanes  
having different length alkyl chains. For example the  
coating composition may comprise an alkylsilane having an  
alkyl chain length of 3 carbon units or less (i.e. a C<sub>1-3</sub>  
alkyl) and an alkylsilane having an alkyl chain length of  
10 6 carbon units or more (eg. a C<sub>6-30</sub> alkyl).

The mixture of long and short alkyl chain alkylsilanes  
significantly enhances the hydrophobicity of the resultant  
surface. The present inventors have found that when two  
15 alkylsilanes having substantially different length alkyl  
chains are used, the resultant surface is typically  
superhydrophobic. Without wishing to be bound by theory,  
it is believed that the different alkylsilanes have a  
tendency to agglomerate together, thereby forming  
20 hydrophobic nanoparticles having different sizes and  
imparting a greater nanoscale roughness to the resultant  
surface, increasing the hydrophobicity of the surface.

When a mixture of a short alkyl chain alkylsilane and a  
25 long alkyl chain alkylsilane is used, the ratio of short  
alkyl chain alkylsilane : long alkyl chain alkylsilane  
may, for example, range from about 7:1 to about 1:1,  
preferably 5:1, by weight.

30 Suitable long alkyl chain alkylsilanes include  
octyltriethoxysilane, octyltrimethoxysilane,  
decyltriethoxysilane, decyltrimethoxysilane,  
dodecyltriethoxysilane, and dodecyltrimethoxysilane.

- 15 -

The coating composition comprising one or more tri-functional alkylsilane(s) may also comprise mono- or di-functional alkylsilanes.

5 Polysiloxane compounds are intrinsically hydrophobic because of the large number of siloxane bonds, and thus contribute to the hydrophobicity of the resultant surface. The polysiloxane compound must be capable of reacting with the alkylsilane(s). Typically, the terminal ends of the  
10 polysiloxane compound have a functional group that can react with the alkylsilane(s), for example, the polysiloxane compound can have terminal hydroxy or silanol groups. Alternatively, these functional groups may be present at intervals along the polymer chain.

15

During curing of the composition, the polysiloxane compound may bind to hydrophobic nanoparticles formed by the hydrolysis and condensation of the alkylsilanes, or to an alkylsilane which then binds to other alkylsilanes to  
20 form a hydrophobic nanoparticle, thereby linking the hydrophobic nanoparticles together.

The polysiloxane compound can also typically react with functional groups on the microstructured surface, linking  
25 the hydrophobic nanoparticles formed by the hydrolysis and condensation of the alkylsilanes to the microstructured surface. The polysiloxane compound thus contributes to the durability and elasticity of the resultant hydrophobic or superhydrophobic surface.

30

Suitable polysiloxane compounds include hydroxy terminated polydimethylsiloxane (PDMS), hydroxy terminated polydimethylsiloxane-co- polyphenylmethylsiloxane, hydroxy



- 16 -

terminated vinylsiloxane polymer, hydroxy terminated polydiphenylsiloxane, hydroxy terminated polyphenylmethylsiloxane, vinylmethoxysiloxane homopolymer (terminated with a methoxy group at intervals along the  
5 polymer chain), polytrifluoropropylmethylsiloxane (silanol terminated), and vinylmethylsiloxane-dimethylsiloxane copolymer (silanol terminated). The coating composition may comprise a mixture of two or more polysiloxane compounds.

10

The organic solvent may be any inert organic solvent and is preferably ethyl acetate. Other inert organic solvents can be used, however, for example butyl acetate, toluene, xylene, methyl ethyl ketone, acetone, hexane, light  
15 petroleum, diethylether, or tetrahydrofuran.

The catalyst catalyses the condensation reactions, thereby causing the hydrophobic coating to cure more rapidly. Any catalyst commonly used for silane condensation reactions  
20 may be used, for example tin and zinc catalysts such as dibutyltin dilaurate, zinc octoate and tin octoate.

The catalyst (or a different catalyst) may also catalyse the reaction of the alkylsilane with the polysiloxane  
25 compound.

The coating composition may optionally further comprise an adhesion promoter. The adhesion promoter facilitates chemical bonding of the hydrophobic nanoparticles to the  
30 microstructured surface and thus increases the durability of the resultant hydrophobic or superhydrophobic surface. Compounds suitable for use as an adhesion promoter include (3-aminopropyl)triethoxysilane,

- 17 -

(3-aminopropyl)trimethoxysilane and  
glycidylpropyltriethoxysilane.

An example of a coating composition for use in the method  
5 of the present invention may be prepared as described  
below.

The coating composition is prepared by mixing an  
alkylsilane having a short ( $c < 3$ ) alkyl chain, a  
10 polysiloxane compound having terminal hydroxy groups, an  
organic solvent, and catalyst together in a suitable  
ratio, for example, between about 0.1 to about 0.5%  
catalyst by weight of the mixture.

15 The mixture may then be heated to 60°C for 3 to 6hrs. The  
reaction mixture is heated to activate the polysiloxane  
compound, ie. such that the terminal hydroxy groups of the  
polysiloxane compound are substituted by an alkylsilane.  
No other significant reaction of the alkylsilanes occurs  
20 at this time because there is no water present to cause  
hydrolysis of the alkylsilanes. One or more  
alkylsilane(s) having a long ( $c > 6$ ) alkyl chain is/are then  
added to the mixture. The resultant coating composition  
may then be stored in the absence of water or air for some  
25 time before use in the method of the present invention.

The coating composition may be applied to a  
microstructured surface using any technique known in the  
art, for example, painting, spray coating, dip coating or  
30 spin coating. The coating composition is typically  
applied to the microstructured surface in an amount such  
that, on curing, a thin layer of the hydrophobic coating  
having a nanoscale roughness overlays the microstructured

- 18 -

surface, thus resulting in a surface having both nanoscale and microscale roughness.

The amount of coating composition applied to a  
5 microstructured surface may vary, and a suitable amount to form a hydrophobic coating having nanoscale roughness can readily be determined by a person skilled in the art. In general, any amount of coating composition may be applied, provided that the resultant hydrophobic coating does not  
10 cover the microstructure to a thickness such that the resultant surface does not have microscale roughness.

Typically, the coating composition is applied to form a layer of between 0.1 to 1 micron thick, which on drying  
15 forms a hydrophobic coating layer less than 1 micron thick. Because of this thin layer, the hydrophobic coating is essentially transparent. This is advantageous as the method of the present invention can be used to render surfaces hydrophobic without significantly changing  
20 the colour or appearance of the surface, and without significantly reducing the transmission of light through a transparent or translucent substrate.

Once the coating composition has been applied to the  
25 microstructured surface, the composition is cured. Typically, the composition is cured by allowing the composition to dry at room temperature in the presence of air. During the curing, the solvent in the coating composition evaporates, and the composition is exposed to  
30 water from the atmosphere. The alkylsilanes in the coating composition react with this water to form hydrophobic nanoparticles via the modified sol-gel reaction discussed above.

- 19 -

Furthermore, during the curing of the composition, the polysiloxane compound reacts with functional groups on the microstructured surface, thereby linking the hydrophobic nanoparticles to the microstructured surface and enhancing  
5 the durability of the coating.

#### Microstructured surface

The surface to which the coating composition is applied is microstructured, ie. it has a microscale texture or  
10 roughness. Some substrates intrinsically have a microstructured surface. Examples of substrates having surfaces that have an intrinsic microscale roughness include sandstone, some ceramic materials, some cementitious materials and textiles. The nature or extent  
15 of this roughness will depend on the material's composition and processing.

For substrates that do not have an intrinsic microscale roughness, a surface of the substrate may be treated to  
20 form a microstructured surface (ie. a surface having a microscale roughness). Typically, this is achieved by applying a composition to the surface to form a coating having a microstructured surface. The coating is typically formed by applying a composition comprising  
25 microparticles, or smaller particles which react or associate to form microparticles, to the surface. Suitable microparticles include clay particles, cementitious particles, and inorganic oxide particles. The inorganic oxide particles may also be used to impart a  
30 colour to the microstructured surface. Suitable inorganic oxides may be selected from the group consisting of iron oxide red, iron oxide black, iron oxide yellow, iron oxide

- 20 -

brown, iron oxide green, titanium(IV) oxide, chromium oxide green, and mixtures thereof.

The coating composition for forming a microstructured surface may be applied to the surface using any technique known in the art, for example, painting, spray coating, dip coating or spin coating.

For illustrative purposes, a number of examples of compositions for forming a microstructured surface on a ceramic or cementitious substrate are given below.

#### Ceramic coating

A ceramic surface may intrinsically be a microstructured surface. Alternatively, a microstructured surface may be formed on a ceramic substrate by applying a composition containing microparticles of ceramic material to a surface of the substrate to form a microstructured surface on the substrate. Such a composition may be in the form of a slurry comprising:

- (a) clay or grinding microparticles;
- (b) a water miscible solvent, for example an alcohol;
- (c) water; and
- (d) optionally, a water soluble and thermo-degradable polymer.

The slurry may be applied to the surface of, for example, clay work pieces of various shapes and having wet or dry surfaces. The clay work pieces are left to air dry for 3 days, and are then cured in an oven at 1100°C for 24 hrs to fuse the microparticles to the surface, producing a microstructured surface on the pieces.

- 21 -

For example, a microstructured surface may be formed on a ceramic work piece as follows:

- mixing the water and alcohol (in a ratio of from, for example, 0:1 to 3:1) with clay microparticles or grinding microparticles to form a slurry (and optionally adding 1 to 20% wt of a water soluble and thermo-degradable polymer to assist in structuring the surface);
- applying the resultant slurry to a wet or dry surface of the clay work piece;
- leaving the coated clay work piece at room temperature for 3 days, followed by thermal treatment at 1100°C for 24 hrs; and then
- allowing the coated ceramic work piece to cool.

15

After cooling to room temperature, the coating composition capable of forming a hydrophobic coating having a nanoscale roughness may be applied to the ceramic microstructured surface. The coated ceramic microstructured surface may then be cured at room temperature for at least 12 hrs, as discussed above, resulting in a hydrophobic or superhydrophobic ceramic surface.

20

- 25 The surface produced by this method has a roughness in both the micro and nano scales, as well as low surface energy. The surface shows high contact angles ( $>150^\circ$ ) for a water droplet and low contact angle hysteresis ( $<20^\circ$ ). Thus, a water droplet is easily able to bead on the surface and roll off with minimum vibration.
- 30

- 22 -

Such a method may be used to produce hydrophobic or superhydrophobic surfaces on ceramic substrates such as roof tiles, facade tiles and pavers.

5    Cementitious coating

A cementitious surface may intrinsically be a microstructured surface. Alternatively, a microstructured surface may be formed on a cementitious substrate by applying a composition containing microparticles of  
10   cementitious material to a surface of the substrate to form a microstructured surface on the substrate.

A composition for forming a cementitious coating having a microstructured surface may be prepared by incorporating  
15   cementitious microparticles into a modified sol-gel reaction.

Such a composition may be in the form of a slurry comprising:

- 20       (a)     a sol made from the hydrolysis and condensation of alkoxy alkylsilanes in alcohol;  
         (b)     cementitious microparticles; and optionally  
         (c)     a colour oxide.

25   The slurry is applied to a surface, for example, a surface made from a brick or cementitious material such as brick, cement, concrete, mortar, or plaster. Once the resultant microstructured surface has been cured, the coating composition capable of forming a hydrophobic coating  
30   having a nanoscale roughness may then be applied.

Typically, the method for applying such a composition to a surface comprises the steps of:

- 23 -

- preparing the sol by mixing an alkoxy alkylsilane, alcohol and water (acidified to pH=4 by hydrochloric acid) at 60°C for 3 hours;
- mixing the sol with cementitious microparticles and a colour oxide to form a slurry; and then
- applying the slurry to the surface by brushing, rolling or spraying, and then curing the slurry, thereby forming a microstructured surface (alternatively, the slurry can be allowed to set, thereby forming an article having microstructured surfaces which are suitable for applying the coating composition capable of forming a hydrophobic coating having a nanoscale roughness to).

The alkoxy alkylsilane used in the above method may, for example, be methyltrimethoxysilane, methytriethoxysilane, ethyltrimethoxysilane, or ethyltriethoxysilane.

The alcohol may be, for example, ethanol or isopropanol.

Such a method may be used to produce hydrophobic or superhydrophobic surfaces on cementitious substrates such as roof tiles, wall facades, plasterboard, or cementitious surfaces.

#### Textiles

The method of the present invention may be applied to textiles having intrinsic microstructured surfaces, for example, cotton, wool, synthetics and blends, utilising the inherent microstructure of woven fibrous material.

Suitable methods for applying the coating compositions capable of forming a hydrophobic coating having a



- 24 -

nanoscale roughness to textiles include spray and dip coating.

Experiments by the present inventors have indicated that  
5 textile surfaces can be made superhydrophobic without significantly changing their textile feel.

Such a method may be used to produce hydrophobic or superhydrophobic surfaces on textiles used in numerous  
10 items such as tents, furnishings, swimwear, outdoor wear, or umbrellas.

Preferred embodiments of the invention will now be described, by way of example only, with reference to the  
15 following Examples.

#### EXAMPLES

##### Example 1

20

Coating composition capable of forming a hydrophobic coating having a nanoscale roughness

Mix 100 g methyltrimethoxysilane (MTMS), 10 to 200g hydroxy terminated polydimethylsiloxane (PDMS), 50 to  
25 150mL ethyl acetate and stir the mixture at 60°C for 3 to 6 hrs. The mixture is then blended with 10 to 100g of octyltriethoxysilane, 4 to 40g of (3-aminopropyl)trimethoxysilane and 1 to 5g dibutyltin dilaurate (a catalyst).

30

This mixture may be stored in an airtight container (for example, a metal drum or bottle) for a number of months prior to use.

**Example 2**Coating composition capable of forming a hydrophobic coating having a nanoscale roughness

- 5 Methyltrimethoxysilane (MTMS), hydroxy terminated polydimethylsiloxane (PDMS), ethyl acetate and dibutyltin dilaurate (0.1%) were added in the amounts shown below to a large reaction vessel in an inert atmosphere. The mixture was then stirred and heated at 60°C for 3 hours.
- 10 Octyltriethoxysilane and 3-aminopropyltriethoxysilane were then added with stirring.

Material	% (wt)
Methyltrimethoxysilane	45
Polydimethylsiloxane (-OH term.)	4.5
Octyltriethoxysilane	9
ethyl acetate	40
Dibutyltin dilaurate	0.5
3-Aminopropyltriethoxysilane	1

- The resultant coating composition may be stored in an
- 15 airtight container (for example, a metal drum or bottle) for months. Further tin catalyst (0.4%) is added to the composition shortly before applying the composition to a microstructured surface. The mixture of the composition with the tin catalyst may be stored in an airtight
- 20 container for up to a week prior to use.

- 26 -

**Example 3**Microstructured surface formation - using ceramic materials

- 5 Mix 100g of ethanol, 1 to 20g of polyethylene oxide (mw ~1,000), and 200g of clay particles or grindings (microparticle size) to form a slurry. Apply the slurry to a wet surface of a clay workpiece, and then leave the workpiece at room temperature for 3 days. Finally, cure  
10 the workpiece at 1100°C for 24 hrs.

The coating composition described in Example 1 or 2 can then be applied to the microstructured surface of the ceramic workpiece and the coated workpiece is cured at  
15 room temperature for at least 12 hrs.

The surface of the ceramic work piece made by this process is extremely water resistant and exhibits a water contact angle of larger than 165°.

20

**Example 4**Microstructured surface formation - using cementitious material

- 25 100g methyltrimethoxysilane (MTMS), 50 to 400g ethanol, 50 to 100g water (pH = 4, acidified by HCl) are mixed and stirred at 60°C for 3 to 6 hrs. The resultant sol is then blended with cement microparticles, and black oxide in a ratio of 3.5 : 5.8 : 0.7 to form a slurry, which is  
30 applied to a surface of a substrate.

After the slurry has been applied to the surface and cured by heating at 1100°C for 24 hrs, a coating composition

- 27 -

prepared using the method of Example 1 or 2 is applied to the microstructured surface to form a thin film which is 0.1 to 1 micron thick. The resultant surface is then cured in air at room temperature for 8 to 24 hrs.

5

The superhydrophobic surface made by this process is extremely water resistant and exhibits a water contact angle of larger than 165°.

10 **Example 5**Microstructured surface formation - using textiles

Textile material is sprayed with a coating composition prepared using the method of Example 1 or 2 such that it is 0.1 to 1 micron thick. Alternatively, the textile material is immersed in a diluted solution (5 to 20%) of the coating composition. The composition is cured in air at room temperature for 8 to 24 hrs.

20 The superhydrophobic surface made by this process is extremely water resistant and exhibits a water contact angle of larger than 150°.

The present invention may be used to form hydrophobic or superhydrophobic surfaces on a variety of substrates. The method can be used to render surfaces of substrates water proof and resistant to icing and fouling.

25 Although the present invention has been described with reference to particular examples, it will be appreciated by those skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the

30

- 28 -

spirit or scope of the invention as broadly described.  
All such variations and/or modifications are to be  
considered within the scope of the present invention the  
nature of which is to be determined from the foregoing  
5 description.

In the claims which follow and in the preceding  
description of the invention, except where the context  
requires otherwise due to express language or necessary  
10 implication, the word "comprise" or variations such as  
"comprises" or "comprising" is used in an inclusive sense,  
ie. to specify the presence of the stated features but not  
to preclude the presence or addition of further features  
in various embodiments of the invention.

15

- 29 -

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for rendering a microstructured surface of a substrate hydrophobic, the method comprising the steps of:
  - applying to the microstructured surface a coating composition capable of forming a hydrophobic coating having a nanoscale roughness on the microstructured surface; and then
  - curing the composition to form a hydrophobic coating having a nanoscale roughness on the microstructured surface, such that the resultant surface has both nanoscale roughness and microscale roughness.
2. The method as claimed in claim 1, wherein the coating composition comprises one or more tri-functional alkylsilanes, and the hydrophobic coating having a nanoscale roughness is formed by the molecules of the tri-functional alkylsilanes reacting together in a modified sol-gel reaction.
3. The method as claimed in claim 1 or claim 2, wherein the coating composition comprises two or more different tri-functional alkylsilanes, the different alkylsilanes having different length alkyl chains.
4. The method as claimed in claim 3, wherein one of the tri-functional alkylsilanes in the coating composition has an alkyl chain having a length of 3 or less carbon units, and another of the tri-functional alkylsilanes in the coating composition has an alkyl chain having a length of 6 to 30 carbon units.

- 30 -

5. The method as claimed in any one of claims 2 to 4,  
wherein the functional groups of the tri-functional  
alkylsilane(s) are independently selected from the group  
consisting of acetoxy, enoxy, oxime, alkoxy and amino.
- 5 6. The method as claimed in any one of claims 2 to 5,  
wherein the coating composition further comprises a  
polymer that is capable of chemically bonding to the  
tri-functional alkylsilane(s) and to the microstructured  
10 surface.
7. The method as claimed in claim 6, wherein the polymer is  
a polysiloxane polymer.
- 15 8. The method as claimed in any one of claims 2 to 7,  
wherein the coating composition further comprises an  
organic solvent.
9. The method as claimed in claim 8, wherein the organic  
20 solvent is ethyl acetate, butyl acetate, toluene,  
xylene, methyl ethyl ketone, acetone, hexane, light  
petroleum, diethylether, or tetrahydrofuran.
10. The method as claimed in any one of claims 1 to 9,  
25 wherein the composition is applied to form a hydrophobic  
coating between about 0.1 and about 1 micron thick.
11. The method as claimed in any one of claims 2 to 10,  
wherein the composition is cured by allowing the  
30 composition to dry at about 15°C to about 30°C in the  
presence of air.

- 31 -

12. The method as claimed in any one of claims 2 to 10, wherein the composition is cured by allowing the composition to dry at about 60°C to about 80°C in the presence of air.

5

13. The method as claimed in any one of claims 1 to 12, wherein the contact angle of water on the resultant surface is greater than 130°

10 14. The method as claimed in any one of claims 1 to 13, wherein the contact angle of water on the resultant surface is greater than 150°.

15 15. The method as claimed in any one of claims 1 to 14, wherein the contact angle of water on the resultant surface is greater than 160°.

16. A method for rendering a surface of a substrate hydrophobic, the method comprising the steps of:

- 20 - treating the surface of the substrate to form a microstructured surface;
- applying to the microstructured surface a coating composition capable of forming a hydrophobic coating having a nanoscale roughness on the microstructured
- 25 surface; and then
- curing the composition to form a hydrophobic coating having a nanoscale roughness on the microstructured surface, such that the resultant surface has both nanoscale roughness and microscale roughness.

30

17. The method as claimed in claim 16, wherein the surface of the substrate is physically treated to form a microstructured surface.



18. The method as claimed in claim 16, wherein the surface is treated by applying a coating composition to the surface to form a coating on the surface, wherein  
5 the coating has a microstructured surface.
19. The method as claimed in claim 18, wherein the microstructured surface is formed by applying a composition comprising microparticles, or smaller  
10 particles capable of forming microparticles, to the surface.
20. The method as claimed in claim 19, wherein the microparticles are clay microparticles, cementitious  
15 microparticles, or inorganic oxide microparticles.
21. The method as claimed in any one of claims 16 to 20, wherein the composition is applied to form a hydrophobic coating between about 0.1 and about 1 micron thick.  
20
22. A hydrophobic surface produced by the method of any one of claims 1 to 21.
23. A superhydrophobic surface produced by the method of  
25 any one of claims 1 to 21.
24. An article having at least one surface that has been rendered hydrophobic according to the method of any one of claims 1 to 21.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU2005/000042

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int. Cl. <sup>7</sup> : C04B 41/45; C08K 3/34, 5/54, 5/541; C09D 183/04, 183/02, 185/00 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C04B 41/45; C08K 3/34, 5/54, 5/541; C09D 7/12, 183/04, 183/02, 185/00; C23C 26/00; B28B 11/00 - 11/24, 21/00 - 21/98, 19/00; E04F 21/00; D06M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT; JAPIO; USPTO; Espace@net; Keywords - nanoparticl+, microparticl+, hydrophob+, repel+, coat+, microstructur+, silant+, siloxan+, polysiloxan+		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 2003-756616/71, Class A82 F06 G02, WO 2003/066241, (CREAVIS GES TECHNOLOGIE & INNOVATION MBH), 14 August 2003 & WO 2003/066241 See Abstract	1-24
X	Derwent Abstract Accession No. 2003-533524/51, Class A84 E19 F01, DE 10118348, (CREAVIS GES TECHNOLOGIE & INNOVATION MBH), 17 October 2002 & DE 10118348 See Abstract	1-24
X	WO 2002/049980 A (FERRO GMBH [DE]), 27 June 2002, & US 6800354 B2 Whole document	1-24
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 22 February 2005		Date of mailing of the international search report 02 MAR 2005
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  WARREN TAYLOR Telephone No: (02) 6283 2229

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/000042

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2001/014497 A (UNISEARCH LTD et al [AU]), 1 March 2001, & US 6743467 B1 Whole document	1-24
X	US 6287639 B1 (SCHMIDT et al), 11 September 2001 Whole document	1-15, 22-24
X	Derwent Abstract Accession No. 2002-539476/58, Class A82 G02, DE 10051182 A, (NANO X GMBH), 2 May 2002 & DE 10051182 A See Abstract	1-24
X	Patent Abstracts of Japan JP 2003-155411 A (SHINETSU CHEM IND Co Ltd), 30 May 2003 See abstract & JP 2003-155411 (whole document)	1-15, 22-24
X	US 2003/0186066 A (MONKIEWICZ et al), 2 October 2003 Whole document	1-24
X	US 2002/0059974 A (KELLER et al), 23 May 2002 Whole document	1-24
X	US 6649266 B1 (GROSS et al), 18 November 2003 Whole document	1-24
X	Patent Abstracts of Japan JP 2003-128991 A (NIPPON SODA Co Ltd), 8 May 2003 See Abstract & JP 2003-128991	1-15, 22-24

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2005/000042

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
WO	03066241	AU	2003244479	DE	10205007
				EP	1472011
WO	02084013	DE	10118348		
US	6800354	AU	35752/02	CA	2429866
		EP	1347948	US	2002142150
				DE	10063739
				WO	0249980
US	6743467	AU	65497/00	CA	2383234
		NZ	517308	EP	1210396
				WO	0114497
US	6287639	AU	54825/98	AU	55524/98
		BR	9712956	BR	9713084
		CN	1236339	CA	2271310
		EP	0946313	DE	19647368
		PL	333455	EP	0950039
		WO	9822241	ID	18721
				US	6378599
				US	6352610
				WO	9822536
				WO	9822648
DE	10051182				
JP	2003155411				
US	2003186066	DE	10212523	EP	1347024
				JP	2003277683
US	2002059974	DE	10057319	DE	10058131
		EP	1207189	EP	1206976
US	6649266	DE	19917366	EP	1183107
				WO	0062942
JP	2003128991				
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.					
END OF ANNEX					

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record.**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**